(11) Publication number:

0 079 679

A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 82305429.1

2 Date of filing: 12.10.82

(5) Int. Cl.³: C 07 C 7/08 C 07 C 7/04, C 07 C 11/08 C 07 C 11/09, C 07 C 11/167

(30) Priority: 13.10.81 JP 163073/81 13.10.81 JP 163074/81

Date of publication of application: 25.05.83 Bulletin 83/21

(84) Designated Contracting States: GB IT NL

(71) Applicant: NIPPON ZEON CO., LTD. 6-1, 2-chome Marunouchi Chiyoda-ku, Tokyo(JP)

(72) Inventor: Ogura, Shunichiro 20-7, Tokiwadai 1-chome Itabashi-ku Tokyo(JP)

(72) Inventor: Soumai, Masamichi 43-1, Motoohashi 1-chome Totsuka-ku Yokohama-shi Kanagawa-ken(JP)

(74) Representative: Myerscough, Philip Boyd et al, J.A.Kemp & Co. 14, South Square Gray's Inn London, WC1R 5EU(GB)

3 - dist. Nr - extract. dist. C - extract. dist.

(54) Process for separating highly pure butene-1 and butene-2.

(57) A process for separating highly pure butene-2 and butene-1 from a C4 hydrocarbon fraction containing isobutane, n-butane, butene-1, butene-2, and at least one diolefinic hydrocarbon and/or at least one acetylenic hydrocarbon, which comprises (1) as a step A treating the C₄ hydrocarbon fraction with a polar solvent to separate it into a raffinate containing isobutane and n-butane and an extract containing butene-1, butene-2, the diolefinic hydrocarbon and/or the acetylenic hydrocarbon, (2) as a step B introducing the extract from step A into a first distillation column to obtain a fraction containing butene-1, the olefinic hydrocarbon and/or the acetylenic hydrocarbon and purified butene-2, (3) as a step C, introducing the fraction obtained in step B into a second extractive distillation column and treating it with a polar solvent to separate it into a raffinate containing butene-1 and an extract containing the diolefinic hydrocarbon and/or the acetylenic hydrocarbon (or)(2') as a step B,) introducing the extract from step A into a second extractive distillation column and treating it with a polar solvent to separate it into a raffinate containing butene-1 and butene-2 and an extract containing the diolefinic hydrocarbon and/or the acetylenic hydrocarbon, (3') as a step C introducing the reffinate from the step B into a first distillation column to

obtain butene-1 and purified butene-2, and (4) as a step D, introducing the raffinate or butene-1 obtained in step C into a second distillation column to remove a tiny amount of water and obtain purified butene-1.

D - 2. dist.

BEST AVAILABLE COPY

PROCESS FOR SEPARATING HIGHLY PURE BUTENE-1 AND BUTENE-2

This invention relates to a process for separating highly pure butene-1 and butene-2 from a C_4 hydrocarbon fraction containing isobutane, n-butane, butene-1, butene-2 and at least one diolefinic or acetylenic hydrocarbon.

5

10

15

20

25

30

35

Butene-l of high purity is used as a comonomer in the production of ethylene polymers. Butene-l for use in this field is required to have such a high purity as illustrated in Table 1 below.

Butene-1 may be polymerized to obtain polybutene-1 which is particularly suitable as a material for hot water pipes in heating systems, etc. because of its excellent high-temperature stress cracking resistance, high-temperature creep resistance and environmental stress cracking resistance.

Table 1: Composition of butene-1 for use as a comonomer for production of ethylene polymers

Butene-1 more than 99.0% by weight
Butene-2 less than 0.5% by weight
iso-Butene less than 0.5% by weight
n-Butane less than 0.5% by weight
1,3-Butadiene less than 150 ppm
Acetylenes less than 15 ppm
Water less than 10 ppm

Butene-2 is also a good raw material for maleic anhydride. Furthermore, butadiene can be synthesized by the catalytic oxidative dehydrogenation reaction of butene-2 with a catalyst composed of molybdenum oxide or bismuth oxide as a main ingredient. For example, the article written by L. M. Welch of Petrotex Company of U. S. A. (Hydrocarbon Processing, November 1973, pages 131-136) states that the selectivity to 1,3-butadiene is highest with cis-butene-2, and then with trans-butene-2. Separation of a C₄ hydrocarbon fraction by an ordinary distilling method is very disadvantageous from an economic viewpoint because the

boiling points of n-butane and trans-butene-2 are ver close to each other as shown in Table 2. According to the aforesaid article, if the amount of n-butane in butene-2 is less than 14%, it does not particularly exert adverse effects such as a reduction in selectivity. 5 Since, however, n-butane remains unreacted and gets mixed with the reaction product, the inclusion of a large amount of n-butane makes it necessary to use a large-sized reaction apparatus or worsens the efficiency of a device for separating the resulting 1,3-butadiene. 10 Preferably, therefore, n-butane is removed as much as possible prior to the reaction, especially to a content of not more than 5% by weight.

It is an object of this invention therefore to provide at low costs large amounts of butene-1 and butene-2 having a high purity suitable for use in the aforesaid applications and being substantially free from hazardous impurities.

The C_4 hydrocarbon fraction to be treated by the process of this invention usually denotes a product obtained by removing 1,3-butadiene and isobutylene from C4 hydrocarbons formed as by-products in the steam cracking of naphtha, or a product obtained by removing isobutylene from C_4 hydrocarbons formed as by-products in the catalytic cracking of petroleum, but is not limited to these specific examples. of 1,3-butadiene from these C_4 hydrocarbons can be usually carried out by extraction in accordance with the CAA method (the cuprammonium acetate method), or an extractive distillation method using an extracting polar solvent (e.g., dimethylformamide, dimethylacetamide, N-methylpyrrolidone, and acetonitrile). On the other hand, the removal of isobutylene can be effected by a classical extracting method using sulfuric acid, or a recently developed etherification method using an 35 aliphatic alcohol. For example, A. Clementi of ASSORNI (Association for Scientific Research of ENI Group

15

20

25

30

Companies) of Italy reported in Hydrocarbon Processing, December 1979, pages 109-113 that by contacting a mixture of a C_4 hydrocarbon fraction and methanol with an acid catalyst (e.g., an ion exchange resin having a sulfo group), isobutylene is etherified almost completely, and remains in the C_4 hydrocarbon fraction in a concentration of as low as 0.1% or below.

Table 2 illustrates the composition of a C_4 hydrocarbon residue obtained after removing 1,3-butadiene and isobutylene.

5

10

Table 2: Compositions of C₄ hydrocarbon fractions and their solubility in dimethylformamide

Component	Boiling point (OC)	Compositio C, hydroca fraction		Solubility in dimethyl-formamide		
		Catalytic cracking	Steam cracking	(vol/vol/l atm.)		
Propane	-42.1	1.8	0.2	4.0 (25 ⁰ C)		
Propylene	-47.7	1.0	0.3	8.2 (25 ⁰ C)		
iso-Butane	-11.5	42.7	5.3	9.2 (20 ⁰ C)		
n-Butane	- 0.5	12.7	22.6	16.5 (")		
iso-Butene	- 6.6	0.1	0.1	28.0 (")		
Butene-1	- 6.5	17.8	37.4	24.6 (")		
trans-Butene-2	+ 0.3	13.7	15.7	35.5 (")		
cis-Butene-2	+ 3.7	9.9	13.8	51 (")		
1,3-Butadiene	- 4.7	0.3	0.8	83.4 (")		
Methylacetylene	-23.2	-	0.3	85 (")		
1,2-Butadiene	+10.3	-	1.2	160 (")		
Vinylacetylene	_	-	1.8	350 (")		
c ₅ .	-	-	0.5	-		
		100.0	100.0			

The present inventors have found that when a C₄ hydrocarbon fraction having a similar composition to those shown in Table 2 is treated by a process comprising a combination of two extractive distillation

steps using a polar solvent, particularly dimethylformamide (DMF), and two ordinary distillation steps,
it is possible to obtain butene-1 substantially free
from diolefinic and acetylenic hydrocarbons and water
which are det#rimental to its use as a comonomer for
ethylene polymer formation or as a monomer for production of polybutene-1, and simultaneously a cis-butene2/trans-butene-2 mixture suitable as a material for
the production of 1,3-butadiene by oxidative dehydrogenation.

Thus, according to this invention, there are provided two separating and purifying processes.

A first process is achieved by a combination of the following steps A to D.

Step A

5

10

15

20

25

30

35

A C₄ hydrocarbon fraction is subjected to a first extractive distillation operation using a polar solvent to remove isobutane and n-butane as a raffinate and a mixture of butene-1, cis-butene-2, trans-butene-2 and as impurities, diolefinic and/or acetylenic hydrocarbons as an extract.

Step B

The extract obtained in step A is subjected to a first distillation operation to obtain a fraction consisting mainly of butene-1 and diolefinic and/or acetylenic hydrocarbons from the top of the column and a cis-butene-2/trans-butene-2 mixture from the bottom of the column.

Step C

The fraction obtained in step B is subjected to a second extractive distillation operation to remove the diolefinic and/or acetylenic hydrocarbons entrained in butene-1 as an extract, and butene-1 as a raffinate.

Step D

Water remaining in a tiny amount in butene-l is removed by a second distillation operation. Since water forms a minimum boiling azeotrope with butene-l,

it distills out from the top of the column, and purified butene-1 is obtained from the bottom of the column.

A preferred embodiment of the first process is specifically described with reference to a flowsheet shown in Figure 1. A C hydrocarbon fraction containing 5 butene-1, butene-2, etc. is fed into the middle of a first extractive distillation column A-1 having 100 trays through a line 1, and a polar solvent is fed into the distillation column several trays below its top. 10 Thus, a first extractive distillation operation is From the top of the column, isobutane carried out. and n-butane distill out through a line 3. The distillation column can be operated at a column inside pressure of 1 to 15 atmospheres and a column bottom temperature of 100 to 180°C. From the bottom of the 15 column, butene-1, butene-2, diolefinic hydrocarbons and acetylenic hydrocarbons are withdrawn together with the solvent, and are fed into the top of a first stripping column A-2 through a line 4. In the first 20 stripping column A-2, the C_L hydrocarbons are separated from the polar solvent. The first stripping column A-2 can usually be operated at a column inside pressure of 1 to 2 atmospheres and a column bottom temperature coresponding to the boiling point of the solvent at the pressure employed. From the top of the column, 25 butene-1, butene-2, diolefinic hydrocarbons and acetylenic hydrocarbons are taken out through a line 5, pressurized by a compressor 6, and then fed into a first distillation column B through a line 7. Only the polar solvent is withdrawn from the bottom of the first stripping 30 column A-2, and recycled to the column A-1 through a line 8.

The first distillation column B having 100 trays can be operated at a column inside pressure of 1 to 15 atmospheres and a column bottom temperature corresponding to the boiling point of the hydrocarbon mixture at the pressure employed. From the top of

35

the column, butene-1, diolefinic hydrocarbons and acetylenic hydrocarbons are withdrawn through a line 9 and fed into the middle of a second extractive distillation column C-1. From the bottom of the first distillation column B, cis-butene-2 and trans-butene-2 are withdrawn with small amounts of diolefinic and acetylenic hydrocarbons through a line 10.

A polar solvent is fed through a line ll into the second extractive distillation column C-1 having 100 trays at a site several trays below its top, and it is contacted with butene-1 fed into the middle of the column to perform a second extractive distil-The second extractive distillation lation operation. column C-1 can be operated at a column inside pressure of 1 to 15 atmospheres and a column bottom temperature of 100 to 160°C. From the top of the column, highly pure butene-1 is withdrawn through a line 12, and fed into the middle of a second distillation column D. From the bottom of the second extractive distillation column C-1, diolefinic and acetylenic hydrocarbons are withdrawn together with the solvent, and fed into the top of a second stripping column C-2 where the diolefinic and acetylenic hydrocarbons are separated from the solvent. The second stripping column C-2 can usually be operated at a column inside pressure of 1 to 2 atmospheres and a column bottom temperature corresponding to the boiling point of the solvent at the pressure employed. From the top of the second second stripping column C-2, the diolefinic and acetylenic hydrocarbons are discharged through a line From its bottom, only the solvent is withdrawn and recycled to the second extractive distillation column C-1 through a line 15.

The second distillation column D having 30 trays can usually be operated at a column inside pressure of 1 to 15 atmospheres and a column bottom temperature corresponding to the boiling point of the hydrocarbon

5

10

15

20

25

30

35

mixture at the pressure employed. A very small amount of water is taken out from the top of the second distillation column D through a line 16. Highly pure butene-1 as a product is withdrawn from the bottom of the column D through a line 17.

A second process is achieved by a combination of the following steps \boldsymbol{A} to \boldsymbol{D} .

Step A

5

10

15

20

25

35

A C₄ hydrocarbon fraction is subjected to a first extractive distillation operation using a polar solvent to remove isobutane and n-butane as a raffinate and a mixture of butene-1, cis-butene-2, trans-butene-2 and as impurities, diolefinic and/or acetylenic hydrocarbons as an extract.

Step B

The extract obtained in step A is subjected to a second extractive distillation operation using a polar solvent to obtain a raffinate containing butene-1 and butene-2 as main ingredients from the top of the column and a mixture of diolefinic and/or acetylenic hydrocarbons as an extract from the bottom of the column.

Step C

The raffinate obtained in step B is subjected to a first distillation operation to obtain butene-1 from the top of the column and purified butene-2 from the bottom of the column.

Step D

Water remaining in a tiny amount in butene-1 is removed by a second distillation operation. Since at this time water forms a minimum boiling azeotrope with butene-1, it distills out from the top of the column. Purified butene-1 is obtained from the bottom of the column.

A preferred embodiment of the second process is specifically described below with reference to a flowsheet shown in Figure 2. A C_{Δ} hydrocarbon fraction

containing butene-1, butene-2, etc. is fed into the

middle of a first extractive distillation column A-1 having 100 trays through a line 1. A polar solvent is fed into the column several trays below its top through 5 a line 2. Thus, a first extractive distillation operation is carried out. From the top of the column, isobutane and n-butane distill out through a line 3. The column can be operated at a column inside pressure of 1 to 15 atmospheres and a column bottom temperature of 100 to 180°C. From the bottom of the column, butene-1, 10 butene-2, diolefinic hydrocarbons and acetylenic hydrocarbons are withdrawn together with the solvent, and fed into the top of a first stripping column A-2 through a line 4. In the first stripping column A-2, the C, hydrocarbons are separated from the polar 15 solvent. The first stripping column A-2 can usually be operated at a column inside pressure of 1 to 2 atmospheres and a column bottom temperature corresponding to the boiling point of the solvent at the pressure 20 employed. From the top of the column, butene-1, butene-2, diolefinic hydrocarbons and acetylenic hydrocarbons are withdrawn through a line 5, pressurized by a compressor 6, and then fed into a second extractive distillation column B-1 through a line 7. Only the solvent is withdrawn from the bottom of the first stripping column 25 A-2, and recycled to the column A-1 through a line 8. A polar solvent is fed through a line 9 into the second extractive distillation column B-1 having 100 trays at a site several trays below its top, and 30

100 trays at a site several trays below its top, and
30 contacted with butene-1, butene-2, diolefinic hydrocarbons and acetylenic hydrocarbons fed into the middle of the column through the line 7, whereby a second extractive distillation operation is carried out. The second extractive distillation column can be operated at a column inside pressure of 1 to 15 atmospheres and a column bottom temperature of 100 to 160°C. From the top of the second extractive distillation column B-1,

a mixture of butene-1 and butene-2 is withdrawn through a line 10, and fed into the middle of a first distillation column C. From the bottom of the column, diolefinic and acetylenic hydrocarbons are withdrawn together with the solvent, and fed into the top of a second stripping column B-2 where the diolefinic and acetylenic hydrocarbons are separated from the polar solvent. The second stripping column B-2 can usually be operated at a column inside pressure of 1 to 2 atmospheres and a column bottom temperature corresponding to the boiling point of the solvent at the pressure employed. From the top of the column, the diolefinic and acetylenic hydrocarbons are discharged through a line 12. From the bottom of the column, only the solvent is withdrawn and recycled to the column B-1 through a line 13.

5

10

15

20

25

30

35

The first distillation column C having 100 trays can usually be operated at a column inside pressure of 1 to 15 atmosphers and a column bottom temperature corresponding to the boiling point of the hydrocarbon mixture at the pressure employed. From the top of the column, butene-1 is withdrawn through a line 14, and fed into the middle of the second distillation column D. From the bottom of the column, purified cis-butene-2 and trans-butene-2 are withdrawn through a line 15.

The second distillation column D having 30 trays can usually be operated at a column inside pressure of 1 to 15 atmospheres and a column bottom temperature corresponding to the boiling point of the hydrocarbon mixture at the pressure employed. From the top of the column, a very small amount of water is withdrawn through a line 16. Highly pure butene-1 as a product is withdrawn from the bottom of the column through a line 17.

The polar solvent used in this invention may be any of those polar solvents which are generally used

for the extractive distillation of 1,3-butadiene from a C₄ hydrocarbon fraction. Examples include N-alkyl-substituted lower fatty acid amides, furfural, N-methylpyrrolidone, formylmorpholine, and acetonitrile. The N-alkyl-substituted lower fatty acid amides include dimethylformamide, diethylformamide and dimethylacetamide. These amide solvents are preferred for the object of this invention since they have an excellent solubility, an excellent relative volatility and a moderate boiling point in an anhydrous condition. Table 3 shows the relative volatilities of C₄ hydrocarbons in various polar solvents. Among the above-exemplified polar solvents dimethylformamide is most preferred.

10

15

20

25

These polar solvents may be used singly or as a mixture of two or more. Together with the polar solvent, polymerization inhibitors for inhibiting the polymerization of diolefinic and acetylenic hydrocarbons, antioxidants, antifoamers, etc. may be used. Various types of polymerization inhibitors can be used which have the ability to inhibit polymerization and/or to induce chain transfer. Examples include t-butylcatechol, sulfur sodium nitrite, furfural, benzaldehyde, and aromatic nitro compounds. They may be used either singly or as a mixture of two or more.

 $\frac{\text{Table 3}}{\text{Relative volatilities in various polar solvents}}$ (data obtained at 50°C with infinite dilution)

Solvent	Dimethyl- formamide	Diethyl- formamide	N-methylpyr- rolidone
Boiling point (OC)	153	177.5	202
iso-Butane	5.3	5.2	7.25
n-Butane	3.8	3.6	4.30
Butene-1	2.4	2.3	2.60
trans-Butene-2	1.9	1.8	2.00
cis-Butene-2	1.7	1.5	1.63
1,3-Butadiene	1.0	1.0	1.00

The following examples illustrate the present invention more specifically.

Example 1

5

10

15

20

25

30

35

Using the apparatus shown in Figure 1, the following experiment was carried out.

A starting material having the composition shown in Table 4 was fed at a rate of 22.5 kg/hour into the middle of the first extractive distillation column A-1 having 100 trays through line 1, and extractively distilled under the following conditions.

Polar solvent: fed at a rate of 225 kg/hour
Reflux liquid: 22 kg/hour
Pressure of the top of the column: 3.5 kg/cm² (G)
Temperature of the top of the column: 45°C
Temperature of the bottom of the column: 139°C
As a result, a gas having the composition shown in
Table 4 was obtained at a rate of 16.4 kg/hour from
line 5 of the first stripping column A-2. Removal of butanes was achieved nearly completely.

The resulting gas was forced into the middle of the first distillation column B having 100 trays, and distilled at a column top pressure of 3.3 kg/cm² (G) and a column top temperature of 37°C with a reflux ratio of 9. As a result, a butene-2 mixture having the composition shown in Table 4 was obtained at a rate of 7.65 kg/hour from the bottom of the column through line 10.

All of the gas from the top of the column which contained butene-1 as a main ingredient was introduced into the middle of the second extractive distillation column C-1 having 100 trays, and extractively distilled at a column top pressure of 3.3 kg/cm² (G), a column top temperature of 37°C and a column bottom temperature of 145°C using a polar solvent fed at a rate of 60 kg/hour and maintaining the flow rate of the reflux liquid at 8 kg/hour. From the top of the column, butene-1 substantially free from diolefinic and acetylenic hydrocarbons was obtained.

All of the butene-1 thus obtained was introduced into the middle of the second distilling column D having 30 trays to remove water. After operating at a column top pressure of 3.3 kg/cm² (G) and a column top temperature of 37°C, butene-1 having the composition shown in Table 4 and substantially free from water was obtained at a rate of 7.65 kg/hour from the bottom of the column through line 17.

The polar solvent used was a mixture of anhydrous dimethylformamide with 0.1% by weight of nitrobenzene and 0.05% by weight of sodium nitrite.

Table 4
Compositions (% by weight)

Composition	Starting C4 hydro- carbon fraction from line l	Gas from line 5	Butene-2 mixture from line 10	Butene-1 from line 17
iso-Butane	5.8	-	-	-
n-Butane	21.6	1.4	2.6	0.17
Butene-1	37.4	50.82	1.9	99.17
iso-Butene	0.1	0.14	0.0	0.21
trans-Butene-2	19.7	26.8	57.7	0.35
cis-Butene-2	13.2	17.9	36.8	0.10
1,3-Butadiene	1.5	2.0	0.8	85 (ppm)
Methylacetylene	0.6	0.8	0.0	2 (ppm)
Ethylacetylene	0.1	0.14	0.2	1 (ppm)
	100.0	100.0	100.0	100.0

15 Example 2

5

10

Using the apparatus shown in Figure 2, the following experiment was carried out.

A starting material having the composition shown in Table 5 was fed at a rate of 22.5 kg/hour into the middle of the first extractive distillation column A-1 having 100 trays through line 1, and extractively distilled at a column top pressure of 3.5 kg/cm² (G),

a column top temperature of 45°C and a column bottom temperature of 139°C using a polar solvent solvent fed at a rate of 225 kg/hour and maintaining the flow rate of the reflux liquid at 22 kg/hour. As a result, a gas having the composition shown in Table 5 was obtained at a rate of 16.4 kg/hour from the top of the first stripping column. Removal of butanes was achieved nearly completely.

5

20

25

30

35

The gas from the line 5 was forced into the
middle of the second extractive distillation column B-1
having 100 trays at a rate of 16.4 kg/hour, and
extractively distilled at a column top pressure of 3.3
kg/cm² (G), a column top temperature of 40°C and a
column bottom temperature of 150°C using a polar solvent
fed at a rate of 110 kg/hour and maintaining the flow
rate of the reflux liquid at 16 kg/hour. As a result,
a butene-1/butene-2 mixture substantially free from
diolefinic and acetylenic hydrocarbons was obtained from
the top of the column at a rate of 15.3 kg/hour.

All of the mixture was introduced into the middle of the first distillation column C having 100 trays, and distilled at a reflux ratio of 9, a column top pressure of 3.3 kg/cm² and a column top temperature of 37°C. As a result, butene-2 having the composition shown in Table 5 was obtained at a rate of 7.2 kg/hour from the bottom of the column through line 15. From the top of the column, butene-1 was obtained at a rate of 8.0 kg/hour.

All the butene-1 thus obtained was introduced into the middle of the second distillation column D, and distilled at a column top pressure of 3.3 kg/cm² (G) and a column top temperature of 37°C. As a result, highly pure butene-1 having the composition shown in Table 5 and being substantially free from water was obtained from the bottom of the column through line 17.

The polar solvent used was a mixture of anhydrous dimethylformamide with 0.1% by weight of

nitrobenzene and 0.05% by weight of sodium nitrite. Table 5

Composition (% by weight)

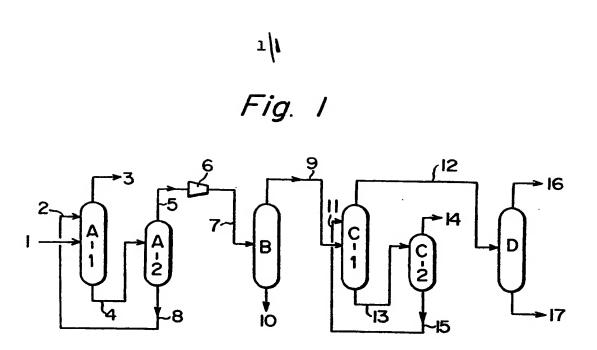
Composition	Starting C4 hydro- carbon fraction from line 1	Gas from line 5	Butene-2 from line 15	Butene-l from line 17	
isc-Butane	5.8	-	-	-	
n-Butane	21.6	1.4	2.7	0.14	
Butene-1	37.4	50.82	1.9	99.30	
iso-Butene	0.1	0.14	0.0	0.20	
trans-Butene-2	19.7	26.8	57.5	0.28	
cis-Butene-2	13.2	17.9	37.9	0.08	
1,3-Butadiene	1.5	2.0	20 (ppm)	72 (ppm)	
Methylacetylene	0.6	0.8	0 (ppm)	2 (ppm)	
Ethylacetylene	0.1	0.14	2 (ppm)	1 (ppm)	
	100.0	100.0	100.0	100.0	

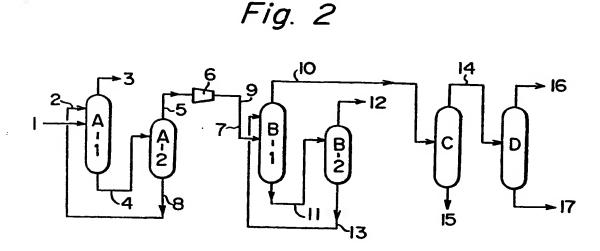
CLAIMS

- 1. A process for separating highly pure butene-2 and highly pure butene-1 substantially free from diolefinic and acetylenic hydrocarbons from a C₄ hydrocarbon fraction containing isobutane, n-butane, butene-1, butene-2, and at least one diolefinic hydrocarbon and/or at least one acetylenic hydrocarbon, which comprises
- (1) as a step A (a first extractive distillation step), treating the C₄ hydrocarbon fraction with a polar solvent in a first extractive distillation column to separate it into a raffinate containing isobutane and n-butane as main ingredients and an extract containing butene-1, butene-2, the diolefinic hydrocarbon and/or the acetylenic hydrocarbon as main ingredients,
- (2) as a step B (a first distillation step), introducing the extract from step A into a first distillation column to obtain a fraction containing butene-1, the olefinic hydrocarbon and/or the acetylenic hydrocarbon as main ingredients from the top of the column and purified butene-2 from the bottom of the column,
- (3) as a step C (a second extractive distillation step), introducing the fraction obtained in step B containing butene-1, the diolefinic hydrocarbon and/or the acetylenic hydrocarbon as main ingredients into a second extractive distillation column and treating it with a polar solvent to separate it into a raffinate containing butene-1 as a main ingredient and an extract containing the diolefinic hydrocarbon and/or the acetylenic hydrocarbon as main ingredients, and
- (4) as a step D (a second distillation step), introducing the raffinate obtained in step C into a second distillation column to remove an azeotrope of water from the top of the column and obtain purified butene-1 from the bottom of the column.

- 2. A process for separating highly pure butene-2 and highly pure butene-1 substantially free from diolefinic and acetylenic hydrocarbons from a C₄ hydrocarbon fraction containing isobutane, n-butane, butene-1, butene-2, and at least one diolefinic hydrocarbon and/or at least one acetylenic hydrocarbon, which comprises
- (1) as a step A (a first extractive distillation step), treating the C₄ hydrocarbon fraction with a polar solvent to separate it into a raffinate containing isobutane and n-butane as main ingredients and an extract containing butene-1, butene-2, the diolefinic hydrocarbon and/or the acetylenic hydrocarbon as main ingredients,
- (2) as a step B (a second extractive distillation step), introducing the extract from step A into a second extractive distillation column and treating it with a polar solvent to separate it into a raffinate containing butene-1 and butene-2 as main ingredients and an extract containing the diolefinic hydrocarbon and/or the acetylenic hydrocarbon as main ingredients,
- (3) a step C (a first distillation step), introducing the raffinate from the step B into a first distillation column to obtain butene-1 from the top of the column and purified butene-2 from the bottom of the column, and
- (4) as a step D (a second distillation step), introducing butene-1 from step C into a second distillation column to remove an azeotrope of water from the top of the column and obtain purified butene-1 from the bottom of the column.
- 3. A process according to claim 1 or 2 wherein the polar solvent used in the first and second extractive distillation steps is an N-alkyl-substituted lower fatty acid amide.

- 4. A process according to claim 3 wherein the polar solvent is dimethylformamide.
- 5. Use of a purified butene-1 from a process as claimed in any one of claims 1 to 4 in the production of ethylene/butene-1 copolymers or polybutene-1.
- 6. Use of a purified butene-2 from a process as claimed in any one of claims 1 to 4 in the production of 1,3-butadiene by oxidative dehydrogenation.





C R HANGH MA CPA
JA G COLLER MA CPA
T J WALLANDS MA CPA
D L CANNON MA CPA
H FRELLY CPA
W GF ALLEN BA CPA
D M GOLDH B SC CPA
D M GOLDH B SC CPA
P B MYERSCUIGH MA CPA
P G A ELLS JONES MA CPA, MITMA
R J BARLON, BSC CPA
A M SENOR, MA CPA
B SENTHAM, MA CPA
M LB AYERS, B SC CPA
A D OVERN, MA CPA
G C WOODS MA CPA
G T EW'S MITMA
T GRAMAM, LB G
S PERRYMAN

J.A. KEMP & CO.

CHARTERED PATENT AGENTS EUROPEAN PATENT ATTORNEYS TRADE MARK AGENTS 0079679

14 SOUTH SQUARE GRAY'S INN LONDON WC1R 5EU TELEPHONE 01-405 3292 FAX 01-242 8832 (KALLE/RICOH 8032) CABLES KEMPATENT TELEX NO. 23676

MUNICH OFFICE

WIDENMAYERSTRASSE 36 8000 MUNCHEN 22 TELEPHONE (89) 48 30 09 TELECOPIER (89): 48 30 09 CABLES KEMPAT AUNICHEN TELEX 52/28/49 (EUPAL)

9 February 1983

European Patent Office, Branch at the Hague, Receiving Section, P.B. 5818 Patentlaan 2, 2280 HV Rijswijk ZH, Netherlands.

Dear Sirs,

Printe reply to LONDON street

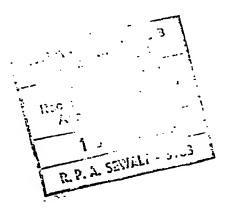
European Patent Application No. 82305429.1 NIPPON ZEON COMPANY LIMITED Our Ref: N/35698 PBM/SJ

I wish to request correction of line 19 of claim 1 by replacement of "olefinic" by "diolefinic" under the provisions of Rule 88 EPC. The need for this correction will be apparent from lines 3, 5 and 13 of claim 1, which all correctly refer to a diolefinic hydrocarbon.

Please acknowledge receipt of this letter by means of the postcard provided.

Yours faithfully,)
P.B. MYERSCOUGH,
(J.A. KEMP & CO.)

The request for correction is allowed under R. SS EPC / who was prime to be steed on the points / MALL SIM (INCLEDED ON MERCETVING SECTION SECTION







EUROPEAN SEARCH REPORT

EP 82 30 5429

	DOCUMENTS CONSI	DERED TO BE	RELEVANT						
Category	Citation of document with of releva	indication, where appro int passages	priate,		elevant claim				OF THE m. Cl. ³)
A	GB-A-2 068 408 FRANCAIS DU PETR			1		C	07 07 07	CCCC	7/04 11/08 11/09
A	GB-A- 881 597 PRODUCTS) * claim 1 *	(UNIVERSAL	OIL	1		С	07	С	11/16
A	US-A-2 993 841 * claim 1 *	 (D.N. SARNO))	4					
A	US-A-2 963 522 * claim 1 *	(J.R. COBB)		6					
:									
					-				IELDS nt. Cl. ³)
						0000	07 07 07 07	00000	7/04 7/08 11/08 11/09
	The present search report has b	oeen drawn up for all clai	ms.						
	Place of search BERLIN	Date of completic 06-01			KNAAC		amine	ır	
Y : F	CATEGORY OF CITED DOCL particularly relevant if taken alone particularly relevant if combined we locument of the same category echnological background non-written disclosure intermediate document		T: theory or pr E: earlier pate after the fill D: document c L: document c 8: member of document	ng d cited cited	late I in the appl I for other n	icatior easons) ;		

THIS PAGE BLANK (USPTO)

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

SKEWED/SLANTED IMAGES

COLOR OR BLACK AND WHITE PHOTOGRAPHS

GRAY SCALE DOCUMENTS

LINES OR MARKS ON ORIGINAL DOCUMENT

REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

OTHER:

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)